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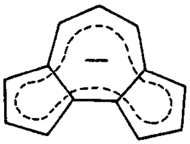
A NEW CATA-CONDENSED NONALTERNANT TETRACYCLIC HYDROCARBON AZULENO[2,1-e]AZULENE

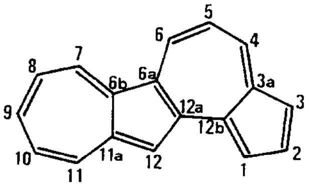
Zen-ichi Yoshida,* Mitsuhiro Shibata, Eiji Ogino and Toyonari Sugimoto
Department of Synthetic Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan

Summary: The titled compound is synthesized from cyclopent[e]azulenide by applying Ziegler-Hafner's azulene synthesis. The ^{1}H- and ^{13}C-NMR spectra indicate large contribution of the structure composed of two azulene-unit (10π) and some contribution of the polarized structure with cyclopentadienyl anion and cycloheptatrienyl cation structures at the terminal 5- and 7-membered rings to the ground state.

It is an important subject to elucidate the π-conjugation mode of cata condensed nonalternant polycyclic π-systems having more than one (4n+2)π conjugation loop. Very recently, we have synthesized cyclopent[e]azulenide (**1**), cyclopentadienide cata-condensed azulene and proved the significant contribution of peripheral 14π conjugation.[1] In this communication, we wish to report the synthesis of azuleno[2,1-e]azulene (**2**),[2] a new cata-condensed nonalternant tetracyclic hydrocarbon and its π-conjugation mode.



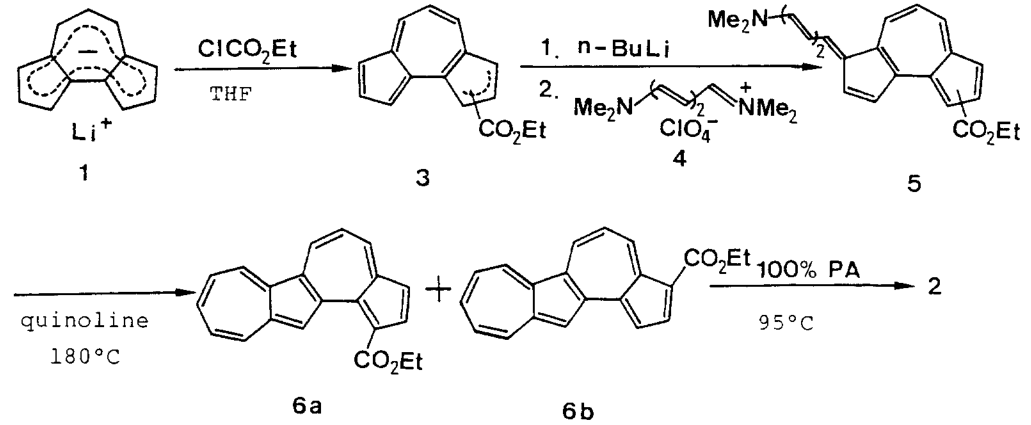
1



2

The synthetic route of **2** is shown in Scheme.[3] Thus, lithium cyclopent[e]azulenide (**1**)[1] reacted with chloroethylcarbonate in THF at -30°C to afford a mixture of 1- and 3-carboethoxy cyclopent[e]azulenes (**3**), which was treated with n-buthyllithium and then with dimethyl-[5-dimethylamino-pentadiene-(2,4)-ylidene]-ammonium perchlorate (**4**)[4] in pyridine-THF to give 3-fulvene derivative (**5**) as a blue solid. Heating of **5** in quinoline at 180°C for 3h, followed by column chromatography (silica gel, dichloromethane) afforded 1-carboethoxy- (**6a**: mp. 104-106°C) and 3-carboethoxy- (**6b**: mp. 181-183°C) azuleno[2,1-e]azulenes[5] as greenish brown crystals in 2% and 6% yields from **1**, respectively. Treatment of **6a** (**6b**) with 100% phosphoric acid

Scheme



at 95°C gave the titled compound (2) in 55%(79%) yield as greenish brown crystals (mp. 143-145°C): The 400 MHz ^{1}H-NMR spectrum ($CDCl_3$, ppm)δ 8.58(d, 1H, H_4 or H_6, J=10.5Hz), 8.41(d, 1H, H_7 or H_{11}, J=8.2Hz), 8.39(d, 1H, H_4 or H_6, J=9.0Hz), 8.07(d, 1H, H_7 or H_{11}, J=10.5Hz), 7.96(s, 1H, H_{12}), 7.95(dd, 1H, H_1 or H_3, J=4.0, 1.4Hz), 7.75(t, 1H, H_2, J=4.0Hz), 7.46(dd, 1H, H_1 or H_3, J=4.0, 1.4Hz), 7.32(dd, 1H, H_9, J=9.4, 8.3Hz), 7.27(dd, 1H, H_8 or H_{10}, J=9.4, 8.2Hz), 7.16(dd, 1H, H_5, J= 10.5, 9.0Hz), 7.15(dd, 1H, H_8 or H_{10}, J=10.5, 8.3Hz). The average chemical shift (δ_{av} = 7.79ppm) is close to that of azulene (7.45ppm)[6], and quite different from[7] that of outer protons of [18]-annulene (9.03ppm).[8] In addition, the observed coupling constants between neighboring protons ($J_{7,8}$, $J_{10,11}$=8.2, 10.5Hz; $J_{8,9}$, $J_{9,10}$=8.3, 9.4Hz; $J_{4,5}$, $J_{5,6}$=9.0, 10.5Hz) indicate the small bond alternation at C_7-C_8-C_9-C_{10}-C_{11} and C_4-C_5-C_6 moieties. From the comparison of the ^{13}C-NMR spectrum of 2 with that of azulene, the chemical shifts of two azulene rings of 2 ($C_{7\sim11}$, 11a,12,12a,6a,6b (r_1) and $C_{1\sim3}$,3a,4∿6,6a,12a,12b (r_2)) is shown to be close to those of azulene itself, suggesting the predominant contribution of two azulene type 10π conjugations rather than peripheral 18π conjugation.[9]

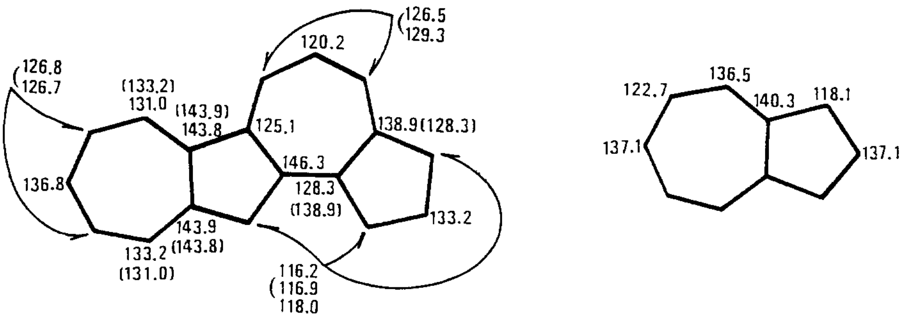
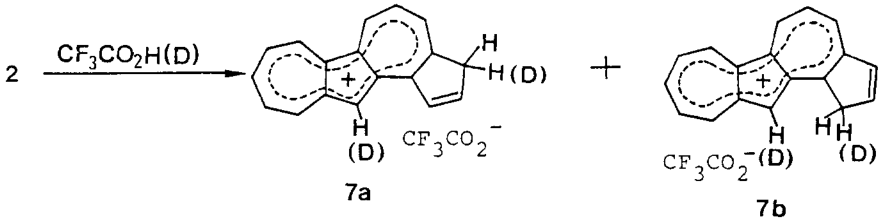


Fig. 1 ^{13}C-NMR spectral data for 2 and azulene[6] ($CDCl_3$, δ[ppm]).

In the ^{13}C-NMR spectra of both compounds, the carbon signals of cyclopentadienyl ($C_{1\sim3,3a,12b}$) and cycloheptatrienyl rings ($C_{6b,7\sim11,11a}$) of **2** appear at the higher and lower magnetic fields respectively compared with those of azulene. This indicates the some contribution of polarized structure with cyclopentadienyl anion and cycloheptatrienyl cation at the terminal 5- and 7-membered rings. In the electronic spectrum of **2** in dichloromethane the absorption bands appear at 246nm(logε=4.14), 276(4.05), 324(4.22), 336(4.20), 390(4.15), 414(4.40) and 438(4.50). The longer wave absorption continues to ca. 850nm, where azulene (<700nm) has no absorption band.



In trifluoroacetic acid **2** was protonated to form a reddish purple solution[10] containing a mixture of 3H- and 1H-azuleno[2,1-e]azulenium ion (**7a** and **7b**, **7a**:**7b**=3:1).[11] When used d_1-trifluoroacetic acid, the H-D exchange of H_{12} proton occured simultaneously for both cations.[12] Therefore, it is considered that the protonation initially occur at C_{12} to give 12H-azuleno-[2,1-e]azulenium ion, which rapidly isomerizes to thermodynamically stable ions **7a** and **7b**.

References and Notes

1. Z. Yoshida, M. Shibata, and T. Sugimoto, Tetrahedron Lett., 4584 (1983).
2. B.A. Hess,Jr, and L.J. Schaad, J. Org. Chem., 36, 3418 (1971).
3. Although the reaction of **1** with **4** gives fulvene derivative (**8**) corresponding to **5**, **8** polymerized in quinoline at 180°C to give no cyclized product.
4. H.E. Nikolajewski, S. Dähne, and B. Hirsh, Chem. Ber., 100, 2616 (1967).
5. 400 MHz ^{1}H-NMR(CDCl$_3$, ppm) **6a**:δ 8.97(s, 1H, H_{12}), 8.85(d, 1H, H_4 or H_6, J=9.8Hz), 8.56(d, 1H, H_7 or H_{11}, J=8.3Hz), 8.54(d, 1H, H_7 or H_{11}, J=8.6Hz), 8.22(d, 1H, H_4 or H_6, J=9.8Hz), 8.12(d, 1H, H_2, J=4.5Hz), 7.5∼7.2(m, 3H, $H_{8,9,10}$), 7.35(t, 1H, H_5, J=9.8Hz), 7.33(d, 1H, H_3, J=4.5Hz), 4.51(q, 2H, $CO_2\underline{CH_2}CH_3$, J=7.1Hz), 1.50(t, 3H, $CO_2CH_2\underline{CH_3}$, J=7.1Hz); **6b**:δ 9.78(d, 1H, H_4, J=9.7Hz), 8.79(d, 1H, H_7 or H_{11}, J=10.2Hz), 8.56(d, 1H,

H_6, J=8.7Hz), 8.36(d, 1H, H_2, J=4.0Hz), 8.16(d, 1H, H_7 or H_{11}, J=11.0Hz), 8.03(s, 1H, H_{12}), 7.83(d, 1H, H_1, J=4.0Hz), 7.50(dd, 1H, H_5, J=10.2, 9.7 Hz), 7.43(dd, 1H, H_9, J=9.7, 8.2Hz), 7.36(t, 1H, H_8 or H_{10}, J= 9.7Hz), 7.24(dd, 1H, H_8 or H_{10}, J=10.9, 8.2Hz), 4.45(q, 2H, $CO_2\underline{CH_2}CH_3$, J=7.1Hz), 1.47(t, 3H, $CO_2CH_2\underline{CH_3}$, J=7.1Hz). As the structure of **6a**, either azuleno[2,1-e]- or azuleno[1,2-e]-azulene is possible. However **6a** was assigned as the former one based on a remarkably down field shift of H_{12} (**6a**, 8.98; **6b**, 8.03ppm) due to the magnetic anisotropy effect of carboethoxy group in the ^{1}H-NMR spectrum. Since decarboxylation of **6b** gave **2**, it was determined that **6b** is 3-carboethoxy isomer of **6a**.

6. J.R. Llinas, D. Roard, M. Derbesy, and E.J. Vincent, Can. J. Chem., 53, 2911 (1975).

7. The ring current induced on each π-conjugation loop in polycyclic conjugated hydrocarbons is propotional to the area of the π-conjugation loop: see J.A. Pople, and K.G. Untch, J. Amer. Chem. Soc., 88, 4811 (1966); J. Aihara, J. Amer. Chem. Soc., 101, 5913 (1979). Therefore, if 18π-conjugation mainly contributes in **2**, much lower magnetic field shift should be observed.

8. L.M. Jackman, F. Sondheimer, Y. Amiel, D.A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A.A. Bothner-By, J. Amer. Chem. Soc., 84, 4307 (1962).

9. This is supported from the estimation of resonance energy of constituent rings (RRE) using Aihara's (βω'ω") method: J. Aihara, private communication (1984), RRE of **2** is as follows: (r_1) 0.066, (r_2) 0.071, (peripheral 18π ring) 0.040.

10. The UV spectrum of a mixture of **7a** and **7b** appears at 514, 372, 358, 332nm. (cf. reference 12)

11. 400 MHz ^{1}H-NMR($CDCl_3$-CF_3CO_2H, ppm) **7a**:δ 9.73(d, 1H, H_4 or H_6, J=9.8Hz), 9.70(d, 1H, H_7 or H_{11}, J=9.5Hz), 9.02(d, 1H, H_7 or H_{11}, J=10.4Hz), 8.80(d, 1H, H_4 or H_6,J=9.8Hz), 8.46(t, 1H, H_9, J=9.5Hz), 8.41(s, 1H, H_{12}), 8.33(t, 1H, H_5, J=9.8Hz), 8.28(t, 1H, H_8 or H_{10}, J=9.5Hz), 8.20(dd, 1H, H_8 or H_{10}, J=10.4, 9.5Hz), 8.04(dd, 1H, H_1, J=5.5, 0.7Hz), 7.82(dt, 1H, H_2, J=5.5, 1.8Hz), 4.28(t, 2H, H_3, J=1.5Hz); **7b**:δ 9.66(d, 1H, H_4 or H_6, J=9.3Hz), 9.46(d, 1H, H_7 or H_{11}, J=8.7Hz), 8.79(d, 1H, H_7 or H_{11}, J=10.1Hz), 8.78(d, 1H, H_4 or H_6, J=10.1Hz), 8.48(t, 1H, H_9, J=9.8Hz), 8.15(s, 1H, H_{12}), 8.16$\sim$8.06(m, 3H, $H_{5,8,10}$), 7.43(bs, 2H, $H_{2,3}$), 4.44(bs, 2H, H_1).

12. On the contrary, the H_{11} proton of cyclohept[a]azulenium ion is reported not to be dueterated in d_1-trifluoroacetic acid.[13]

13. M. Yasunami, T. Amemiya, and K. Takase, Tetrahedron Lett., 69 (1983).

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